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Plasmonic Nanomaterials Based on Metal-Coated Porous Silicon: Fabrication, Characterization and Application in Biosensing

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Abstract

After polymers, silicon is one of the dominating master material for fabrication of nanostructures of noble metals showing surface-enhanced Raman scattering (SERS) activity. Popularity of the silicon templates is caused by its compatibility with basic steps of well-established microelectronic technology making production of the SERS-active substrates easy to control and cost-effective. As a template for the SERS-active substrates silicon is mostly used in different porous forms, which facilitate creating a rich family of metallic nanostructures possessing surprisingly prominent increase of Raman signal from the molecules adsorbed on their surface. In this presentation progress in design, fabrication, characterization, and biosensing application of SERS-active substrates based on porous silicon, including metallic nanoparticles, dendrites, and nanovoids is comprehensively reviewed.

1. Introduction

SERS-spectroscopy is now considered as one of the prospective techniques to detect and study bioorganic molecules for analysis in medicine, pharmacy, forensic science, and other areas essential for human life [1]. SERS phenomena is observed when analyte molecules are located on the surface of particles of coinage metals called SERS-active substrates. Templating is one of the most popular approaches to fabricate such substrates. For example, papers on the formation of the SERS-active substrates using template of porous silicon (por-Si) makes up 15–20% of the total number of publications on the SERS-spectroscopy. This porous material presents a quasi-ordered array of silicon crystallites separated by pores. An attractiveness of por-Si for the SERS-spectroscopy is primarily due to ability to easily and accurately tune the geometry and size of its structural parameters while formation process. A variety of the morphological family of por-Si, which includes arrays of micro-, meso- and macrometer pores, both well-ordered in cylindrical channels or randomly arranged, allows us to create a wide range of the SERS-active structures of metals. For the first time, the idea of using por-Si as a template for formation of the SERS-active substrates appeared in the early 2000s [2]. The authors proposed to cover an internal surface of the porous layer with noble metal film. An appropriate goal was to flow the analyte solution through the metal-coated por-Si and record the SERS-spectra of the molecules captured by the nanoscale pores. This patent application has initiated the intensive study and development of the SERS-active substrates based on por-Si. A goal to review research works on using por-Si as a template for variety of SERS-active metallic nanostructures from the idea to recent progress is pursuing in the present report.

2. What is porous silicon?

Por-Si is an artificial morphological form of nanostructured silicon, which possesses unique physical and chemical properties, which are determined by a network of nanosized pores in the crystalline matrix of silicon and the developed internal surface of these pores. It is more often fabricated by anodic electrochemical etching of monocrystalline silicon in HF-based electrolytes. Parameters of the porous layer, such as the porosity, thickness, size, and structure of the pores depend on a type of the initial monocrystalline silicon and the anodizing regimes. Por-Si is classified depending on the diameter its pores: microporous (< 2 nm), mesoporous (2–50 nm), and macroporous (> 50 nm). All the types of por-Si are characterized by highly developed surfaces facilitating deposition of metallic nanostructures showing SERS-activity. The micropor-Si has been very rarely used for the fabrication of SERS-active nanostructures due to poor mechanical strength. Mesopor-Si is the most popular template for the fabrication of the SERS-active substrates since it combines good mechanical strengths, nanoscale pores, and morphology reproducibility.

3. Fabrication and structure of SERS-active substrates based on porous silicon

The family of the SERS-active nanostructures formed by metal deposition on por-Si is very rich and includes metallic nanoparticles or polydisperse particles, dendrites, and nanovoids [3] (Fig. 1). The SERS-active substrates formed on por-Si have solid bases provided by the underlying silicon wafer, which is very important for the final user because this kind of substrates is favorable for practical applications. Moreover, the silicon basis opens an opportunity to integrate the SERS-active substrates with other devices on the single silicon wafer.

Nanostructures of noble metals (e.g. Ag, Au) that are perfect for the SERS effect can be formed on por-Si by different methods such as thermal decomposition, immersion deposition, deposition from colloids, evaporation, sputtering, physical vapor deposition, pulsed laser deposition, chemical deposition, and electrochemical plating [4]. The immersion technique is the most popular one for the metal coating of por-Si. More precisely, about 60% of the SERS-active substrates based on por-Si have been formed by immersion deposition. Thermal decomposition deserves attention as it was one of the first reported methods to form plasmonic structures on porous silicon. The deposition from colloids is not very common because the method usually leads to the non-uniform distribution of metallic nanoparticels on the substrate and undesirable contaminations into the metal coating due to the by-products of colloids preparation. Electrochemical plating is limited by the fast rate of displacement deposition on the silicon nanostructures typical for metals with a positive redox potential including silver and gold.

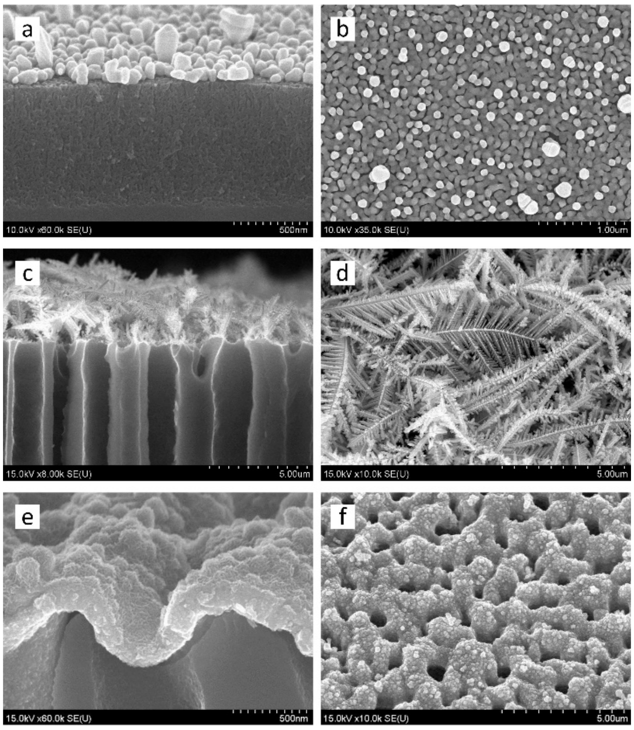

Fig. 1. SEM images of Ag (a, b) nanoparticles on mesopor-Si, (c, d) dendrites on macropor-Si, and (e, f) nanovoids in macropor-Si.

4. Biosensing with SERS-active substrates based on porous silicon

The SERS-active substrates based on por-Si make it possible to perform analyses of the wide range of analytes including the tetrapyrrolic molecules, proteins and peptides, DNA, microRNA, gases, physiological fluids, thiols, and so forth [4]. The femtomolar detection limit has been demonstrated for organic dye R6G, while the enhancement factor for some substrates can rise to an enormous value from 10^8 to 10^{11}.

The paper by Lin and coauthors published in 2004 was one of the first works that reported on the detection of biomolecules with the SERS-active substrates based on porous silicon [5]. The silver dendritic structures were prepared on por-Si by immersion plating and allowed for the adenine detection limit at 10^{-9} M. The SERS-active substrates based on silver-coated por-Si are efficient for the investigation of a number of water-soluble porphyrins.

Giorgis's group has actively published papers on the fabrication of the SERS-active metallized por-Si and its use for the detection of biomolecules at submolar concentrations, including the enzyme horseradish peroxidase [6] or oligopeptides [7]. They developed a detection approach from the immobilization of bioorganic molecules on the surface of the solid substrates made of silver nanoparticles and por-Si to the analyte flowing via the microfluidic system containing the silvered por-Si membrane.

Recently, silvered mesopor-Si was reported as effective SERS-active substrate, which can be applied to the detection of DNA [8], phospholipids [9], and peptides, as well as for the reliable study of their secondary structure [10].

5. Conclusions

The SERS-active substrates based on por-Si have been used for the analysis of a wide range of bioanalytes. The enhancement factor for some substrates can reach 10^{10}–10^{11} [4]. This value is well comparable to that of the best reported SERS-active substrates. The por-Si implementation in SERS-spectroscopy look very promising, especially for the microfluidic chips. This device can solve the problems of non-uniform distribution of analyte on the substrate and its impurities. Today, some SERS-active substrates based on mesopor-Si are commercially available. It can be suggested that the SERS-active substrates based on por-Si can occupy a strong position among the signal improving materials for the SERS-spectroscopy in medicine, biology, forensics, pharmaceutics, analytical chemistry, and other areas which require the highly sensitive analysis of biomolecules.

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